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An IR spectroscopic study of the kinetics of conformational transitions of 1,9,10,11,12,12-hexachloro-4,6-dioxatricyclo[9,2,1,02,8]dodeca-10- ene in solutions

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Abstract

The IR spectra and the exo ⇄ endo conformational equilibrium of 1,9,10,11,12,12-hexachlor--4,6-dioxatricyclo[9,2,1,02,8]dodeca-10- ene (HCA) in carbon disulfide were studied in the temperature range 230-300 K. The difference of the enthalpies was found to be 2.7(2) kJ/mol in favor of the exo conformer. The kinetics of the conformational transition of HCA in acetone-d6 and carbon disulphide was studied in the temperature range 213-220 K. The enthalpies ΔH≠exo and entropies ΔS≠exo of activation of the exo → endo conformational transition were found to be ΔH≠exo = 51(4) and 70(2) kJ/mol and ΔS≠exo = -76(20) and -11(7) J/(mol K) in acetone-d 6 and carbon disulphide, respectively. The ratios between the absorption coefficients of the endo and exo conformer bands (727 cm -1 and 786 cm-1, respectively) were found to be 0.63(9) in acetone-d6 and 0.65(5) in carbon disulfide. The differences of the entropies of the HCA conformers in these solvents [ΔS° = -5(2) J/(mol K)] were determined. The absorption bands were assigned based on the results of quantum-chemical ab initio calculations.